BULLETIN
OF THE
CHEMICAL SOCIETY OF JAPAN

VOL. 1

1926

Editor: Jitsusaburo Sameshima.

Associate Editors: Yasuhiko Asahina, Keijiro Aso, Masumi Chikashige, Shinkichi Horiba, Satoyasu Iimori, Kikunae Ikeda, Fusao Ishikawa, Samuro Kakiuchi, Masao Katayama, Matsusuke Kobayashi, Shigeru Komatsu, Bennosuke Kubota, Riko Majima, Koichi Matsubara, Motooki Matsui, Shinroku Mitsukuri, Hiroshi Nomura, Yukichi Osaka, Keita Shibata, Yuji Shibata, Yoshio Tanaka, Isaburo Wada.

Published by

The Chemical Society of Japan

c/o Faculty of Science, Imperial University of Tokyo.

QD 1
C54
v.1
OHIO STATE
UNIVERSITY

CONTENTS OF VOLUME 1, 1926.

No. 1. JANUARY.

Professor **Kikunae IKEDA** (with a Portrait) 1
Masao KATAYAMA: A Simple Derivation of Planck-Einstein's Formula. 3
Jitsusaburo SAMESHIMA: On the Rate of Flow of Various Gases Through a Porous Wall 5
Toshi INOUE: On the Absorption Spectra of Salt Solutions of Some Rare Earth Elements. 9
Bennosuke KUBOTA and **Taro HAYASHI**: On the Catalytic Hydrogenation of the Carbonyl Group in Aromatic Compounds under Pressure in the Presence of Copper, Part I. 14
Keita SHIBATA: Über die Anhydrisierung von Aminosäuren und Peptiden (Eine Antwort an Herrn Abderhalden) 19

No. 2. FEBRUARY.

Yuzaburo SHIBATA: Deflection of a Flame in the Electric Field . . . 23
Kwantaro ENDO: The Molecular Association of Phenol in Benzene and Water 25
Shinroku MITSUKURI: The Heat of Fusion of Some Organic Solvents Whose Melting Points are Relatively Low 30
Shozo YAMAGUCHI: Catalytic Action of Reduced Copper on Oximes. (On Beckmann's Rearrangement, XV) 35

No. 3. MARCH.

Jitsusaburo SAMESHIMA: Determination of the Density and the Compressibility of Acetylene 41
Satoyasu IIMORI: The Radioactive Manganiferous Nodules from Tanokami, Oomi Province 43
San-ichiro MIZUSHIMA: On the Anomalous Dispersion and Absorption of Electric Waves. I. 47
Shozo YAMAGUCHI: Catalytic Action of Reduced Copper on Oximes. (On Beckmann's Rearrangement. XVI.) 54

No. 4. APRIL.

Heima SINOZAKI, **Ryozaburo HARA** and **Shinroku MITSUKURI**: The Vapour Pressures of Hydrogen Cyanide 59

643494

Isamu NITTA: On the Crystal Structure of Penta-erythritol 62
Shozo YAMAGUCHI: Catalytic Action of Reduced Copper on Pinacones 64
Itizo KASIWAGI: Action de l'Amidure de Sodium sur des Composés Organiques 66
Bennosuke KUBOTA and **Taro HAYASHI**: On the Catalytic Hydrogenation of the Carbonyl Group in Aromatic Compounds under Pressure in the Presence of Copper. Part II. 67
Yuji SHIBATA and **Tei-ichi ASAHINA**: Spectroscopical Study of Amino-acid Anhydrides. I. On the Constitutions of Some Simple Amino-acid Anhydrides 71
Nenokichi HIRAO: On the Terpene and the Sesquiterpene of Mitsubazeri. Preliminary Report 74

No. 5. MAY.

Jitsusaburo SAMESHIMA and **Takeo SUZUKI**: The Action of Protecting Colloids on Mercuric Iodide 81
San-ichiro MIZUSHIMA: On the Anomalous Dispersion and Absorption of Electric Waves. II. 83
Itizo KASIWAGI: Etude de Dérivés du Furfural. I. Condensation du Furfural avec les Cétones Aliphatiques 90
Shirō AKABORI: Synthesis of Methoxy-hydroxy-N-methyl-3.4-dihydroisoquinolinium Salts 96
Shigeru KOMATSU and **Chuichi OKINAKA**: Studies on Proteins. II. Action of Superheated Water on Proteins. I. 102

No. 6. JUNE.

Toshiaki SHIRAI: A Simple Manometer for Measuring Low Pressures. 109
San-ichiro MIZUSHIMA: On the Anomalous Dispersion and Absorption of Electric Waves. III. 115
Masao HIRAI: Melting Curves of the Systems Hydrogen Chloride–Ethyl Ether and Hydrogen Chloride–Acetone 123
Shirō AKABORI: Synthesis of Methoxy-hydroxy-N-methyl-3.4-dihydroisoquinolinium Salts 125
Junkichi MURAI: The Condensation of Resorcinol with Ethylene Dicyanide 129

No. 7. JULY.

Kichimatsu MATSUNO: On the Mechanism of the Substitution Reaction of Trans-dichloro-diethylenediamine Cobaltic Chloride in its Aqueous Solution 133

Tadashi ISHIKAWA: A Study of the Reciprocal Salt Pair: $[K_2, (NH_4)_2]$–$[SO_4, CrO_4]$ at 25°C. 139
San-ichiro MIZUSHIMA: On the Anomalous Dispersion and Absorption of Electric Waves. Part IV. Anomalous Dispersion and Debye's Dipole Theory 143
Itizo KASIWAGI: Etudes de Dérivés du Furfural. II. Etudes Spectrographiques de Quelques Cétones Furyliques 145
Shigeru KOMATSU and **Chuichi OKINAKA:** Studies on Proteins. III. Action of Superheated Water on Proteins. II. 151
Harushige INOUE: On the Catalytic Action of Japanese Acid Earth. I. The Action on a Mixture of Aniline and Methyl Alcohol 157

No. 8. AUGUST.

San-ichiro MIZUSHIMA: On the Anomalous Dispersion and Absorption of Electric waves. Part V. Anomalous Dispersion and Debye's Dipole Theory (Continued) 163
Fusao ISHIKAWA and **Eiichi SHIBATA:** Thermodynamic Studies on Zinc Iodide and Mercurous Iodide 169
Bun-ichi TAMAMUSHI: On the Effects of Gases upon the Surface Tensions of Some Liquids 173
Harushige INOUE: On the Catalytic Action of Japanese Acid Earth. II. The Action on Oximes 177
Yoshisuke UYEDA and **Jinzō KAMON:** Studies on Mercaptals of Sugars. I. Normal Butyl Mercaptals of Sugars 179
Yūichi MAEDA and **Yoshisuke UYEDA:** Studies on Mercaptals of Sugars. II. Normal Propyl Mercaptals of Sugars 181

No. 9. SEPTEMBER.

Shiro YAMAMURA: Freezing Curves of the Systems Benzene-Ether and Benzene-Acetone 183
Bun-ichi TAMAMUSHI: On the Derivation of Adsorption Isotherms . . 185
Jurô HORIUCHI: A Relation between Orthobaric Densities 189
Harushige INOUE: On the Catalytic Action of Japanese Acid Earth. III. The Action on Primary Aliphatic Alcohols 197
Kotaro SHIMO: Some Derivatives of Hydroxyphenylglycine. I . . . 202

No. 10. OCTOBER.

Yohei YAMAGUCHI: Determination of High Temperature by the Effusion and the Transpiration of Gas 209

Satoyasu IIMORI and **Jun YOSHIMURA**: The Radioactivity of the Rubidium Extracted from the Lepidolite and Zinnwaldite of Japan . . 215
Harushige INOUE: On the Catalytic Action of Japanese Acid Earth. IV. The Action on Cyclohexanol and Its Derivatives 219
Kotaro SHIMO: Some Derivatives of Hydroxyphenylglycine. II . . 226
Itizo KASIWAGI: Études de Dérivés du Furfural. III. Sur la Teinte en Passage des Cétones Furyliques 233

No. 11. NOVEMBER.

Satoyasu IIMORI and **Jun YOSHIMURA**: Lepidolite from Nagatori, Chikuzen Province, and the Lithium Content of Japanese Mica 237
Jun YOSHIMURA: Alkali Metals in Beryl from Ishikawa, Iwaki Province 239
Yohei YAMAGUCHI and **Toshimasa TAKEBE**: Studies on the Properties of Diaspore and Bauxite 240
Naoyasu SATA: Die Leitfähigkeitsstudien der Essigsäure in Azeton . . 245
Kashichi ONO: La Déshydration des Alcools Terpéniques Cycliques par la Terre Acide Japonaise (Recherches sur l'Essence de Camphre VI) . 248

No. 12. DECEMBER.

Jiro SASAKI: The Determination of the Helium Content of Some Japanese Minerals 253
Jitsusaburo SAMESHIMA: The True Viscosity and the Colloidal Viscosity 255
Bun-ichi TAMAMUSHI: On the Derivation of Adsorption Isotherms. II. 257
Taku UEMURA, Naomichi YOKOJIMA and **Chinyü TAN**: Spectrochemical Studies of Hydroxyazo-Compounds 260

Author Index to Volume 1 267
Subject Index to Volume 1 271

PROFESSOR KIKUNAE IKEDA.

Kikunae Ikeda was born in Kyoto on October 8th., 1864, as the second son of Harunae Ikeda. His family belonged to the Satsuma Clan, which was one of the most outstanding in introducing western learning in Japan and played most conspicuous role at the time of the Meiji Restoration.

After learning English and eastern classics at several places, young Ikeda entered the preliminary course of the Tokyo University in 1882. Soon he distinguished himself as a most promising student, and graduated the course of chemistry in the College of Science of the University in 1889.

During six years, from 1890 to 1896, he taught in the Higher Normal School. His efforts in improving chemical education in Japan, by introducing rising principles of physical chemistry as the basis, has been widely acknowledged.

In 1896 he was called back to his *alma mater* as an assistant professor in the College of Science, and three years later was sent abroad as a government research fellow. From 1899 to 1901 he studied in the Laboratory of Prof. Ostwald in Leipzig, where many young physical chemists crowded from all parts of the world at that time. After staying for a few months in the Davy-Faraday Research Laboratory of the Royal Institution, London, he returned home and was promoted to the professor of physical chemistry in the Tokyo Imperial University. Soon he took the degree of Rigakuhakushi and directed the chemical institute from 1912 until he retired from the chair on March 1923.

Professor Ikeda was elected a member of the Imperial Academy of Tokyo in 1919. On the establishment of the National Research Council of Japan in 1920, he was elected one of the members, and served as the vice-chairman of its Division of Chemistry from 1921 to 1923. The title of Honorary Professor of the Tokyo Imperial University was bestowed to him on his retirement from the active service in the University. Since the Institute of Physical and Chemical Research was established in 1916, he directed its chemical department until 1921, and still remains there as an active member of the Institute.

Professor Ikeda's works as a physical chemist are chiefly in the field of chemical kinetics and the theory of solutions. As early as 1894 he published a paper on velocity of oxidation of phosphorus. His work with Bredig on the catalytic action of colloidal platinum is well known. He tried an extension of the theory of ideal solution from chemical standpoint, the result of which was published in 1908. Many works on chemical kinetics, enzyme actions and vapour tensions of solutions have been published chiefly in the name of his pupils.

CHEMISTRY HALL LIBRARY FE

Besides physical chemistry, Professor Ikeda has very wide and keen interest in almost every part of chemistry. Especially his success in the practical application of chemistry ought not be passed without notice. He discovered the importance of the salts of glutamic acid and other decomposition products of proteids as the principles of taste in food. "Ajinomoto," verbally taste essence, which is the name given to the product manufactured according to his patent method, is very popular in Japan, being used in household cookings. He applied properly dehydrated acid clay as the adsorbent of moisture. The preparation under the name "Adsole" is now getting great reputation for adjusting humidity in public buildings.

In order to celebrate the sixtieth anniversary of the birthday of Professor Ikeda which was due October last year, his many friends and former pupils have raised a considerable sum of money, which was presented, according to the wish of Professor Ikeda, to the Chemical Society of Japan as a fund for promoting scientific publications. The Society gratefully decided to undertake the publication of short papers or abstracts in European languages, which took the form of this Bulletin.

November, 1925.

Masao KATAYAMA.

A SIMPLE DERIVATION OF PLANCK-EINSTEIN'S FORMULA.

By **Masao KATAYAMA.**

Received November 13, 1925. Published January 28, 1926.

A monatomic solid containing n atoms is considered. It is assumed that each atom oscillates with a fixed frequency ν, its energy being distributed equally for each of three degrees of freedom of atomic motion, and that the energy exchanges for one degree of freedom take place only in integral multiples of a quantum $h\nu$, where h denotes a universal constant. The difference between atoms having different quanta of energy can be regarded, from the standpoint of energetics, similar to the difference of isomeric molecules. The equilibrium between these atoms can be treated in the same way as a chemical equilibrium between isomers.

The energy of each kind of atom in the solid is uniquely determined by ν, and therefore the energy of a system composed of several kinds of atoms is equal to the sum of energy of each kind taken separately. The volume of each atom is constant at a given temperature, and therefore the total volume is also additive. Now a homogeneous mixture in which the energy and volume are additive is known as an ideal solution, the dilute solution being its special case. A chemical equilibrium in such a system follows the law of dilute solutions, and the equilibrium constant can be calculated in the ordinary way.

Let molar fractions of atoms whose energy for one degree of freedom is equal to 0, $h\nu$, $2h\nu$, $3h\nu$,..... $mh\nu$..... be respectively n_0/n, n_1/n, n_2/n, n_3/n..... .....n_m/n..... The equilibrium constant of the transformation of atoms having energy zero to those having energy $mh\nu$ is n_m/n_0. The energy absorbed in the change is $mh\nu N$ for one gram atom, N being Avogadro's constant. Then we have for a small change of absolute temperature T,

$$\frac{d\,ln\frac{n_m}{n_0}}{dT}=\frac{mh\nu N}{RT^2},$$

R : Gas constant.

Since ν is assumed to be constant independent of temperature, the following relation is obtained by integration.

$$ln\frac{n_m}{n_0}=-\frac{mh\nu N}{RT}+C.$$

The integration constant C can be easily known to be zero. For in the limiting case $m=0$, we have

$$n_m = n_0, \quad mh\nu = 0, \qquad \text{so} \quad C = 0.$$

Then the result of integration can be transformed to the following form.

$$\frac{n_m}{n_0} = e^{-\frac{mh\nu}{kT}},$$

k denoting Boltzmann's constant which is equal to R/N.

The number of each kind of atoms, n_0, n_1, n_2, n_3..... n_m....., can now be expressed as follows:

$$n_0,\ n_0 e^{-\frac{h\nu}{kT}},\ \ n_0 e^{-\frac{2h\nu}{kT}},\ \ n_0 e^{-\frac{3h\nu}{kT}},\ \ \ldots\ldots n_0 e^{-\frac{mh\nu}{kT}},\ \ldots\ldots$$

The total number n is equal to the sum of these values:

$$n = n_0(1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + e^{-\frac{3h\nu}{kT}} \ldots\ldots) = n_0 \frac{1}{1 - e^{-\frac{h\nu}{kT}}}.$$

Now the total energy E for all three degrees of freedom is equal to

$$3(0 + h\nu n_1 + 2h\nu n_2 + 3h\nu n_3 + \ldots\ldots),$$

i.e.

$$E = 3h\nu n_0 e^{-\frac{h\nu}{kT}} (1 + 2e^{-\frac{h\nu}{kT}} + 3e^{-\frac{2h\nu}{kT}} + \ldots\ldots).$$

If the mean energy of an atom be denoted with ε, we have

$$E = \varepsilon n = \varepsilon n_0 (1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\ldots).$$

The series in bracket in the former equation for E is evidently equal to the square of that in the latter equation. We have thus by equating these two equations,

$$3h\nu e^{-\frac{h\nu}{kT}} (1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \ldots\ldots) = \varepsilon,$$

i.e.

$$\varepsilon = 3h\nu \frac{e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} = 3 \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

This is the equation of Planck-Einstein for the mean energy of an atom in a monatomic solid.

In the transformation of one gram atom of a certain kind of atom having energy $mh\nu$ to another kind having $m'h\nu$, in the same concentration, the maximum work or the decrease of free energy is equal to $RT \ln \frac{n_{m'}}{n_m}$, while the increase of energy is $(m' - m)h\nu N$. Now it is easily seen from the above results that

$$ln \frac{n_{m'}}{n_m} = -\frac{(m' - m)h\nu}{kT} = -\frac{(m' - m)h\nu N}{RT}.$$

This shows that the change of free energy and total energy is always equal to each other for such transformations. The theory of the action quantum,

i.e. of the energy quantum proportional to frequency, is equivalent to the assumption that the equilibrium of interatomic exchange of energy in a solid can be treated as a chemical equilibrium and Berthelot-Thomsen's principle can be applied to this equilibrium.

Chemical Institute, Faculty of Science, Tokyo Imperial University.

ON THE RATE OF FLOW OF VARIOUS GASES THROUGH A POROUS WALL.[1]

By Jitsusaburo SAMESHIMA.

Received October 27, 1925. Published January 28, 1926.

The velocity of effusion of various gases through a perforated thin plate is expressed by the well known equation $t=k\sqrt{M}$, where t is the time of effusion of the definite volume of gas whose molecular weight is M, and k is a constant. This formula was derived by Schmidt[2] and then verified by Graham,[3] Ramsay and Collie[4] and Donnan.[5] If we use, however, a porous wall such as an unglazed earthenware of compact quality, the above equation can no more be applied as is to be seen from the following experiment.

The apparatus used is shown in Fig. 1. A is a small circular disc of compact unglazed earthenware, the diameter of which is 0.6 cm. and the thickness is 0.15 cm. The disc is attached to an end of a glass tube with sealing wax. The glass tube is connected to a vacuum pump and the pressure is always kept lower than 0.1 mm. The disc is kept at 25° by circulating the water of a thermostat as shown in the figure. The bulb B has a capacity of about 70 c.c. and marked at its upper and lower necks $-C$ and $D-$with lines. A platinum wire attached at the point E on the side-tube serves as the indicator of the constancy of the gas pressure. The gas is put into the vessel B and then the cock F is opened. Now the gas escapes through A and the mercury head goes up. The time which the mercury head requires to pass from D to C is observed. The pressure indicated on the scale H is kept constant during an experiment by raising gradually the mercury reservoir G. The temperature is always kept at 25.°00.

(1) Read before the Chemical Society of Japan, April 4, 1925.
(2) Schmidt, *Gilb. Ann.*, 66 (1820), 39.
(3) Graham, *Phil. Trans.*, 55 (1846), 573.
(4) Ramsay and Collie, *Proc. Roy. Soc.*, 60 (1897), 206.
(5) Donnan, *Phil. Mag.*, [5] 49 (1900), 423.

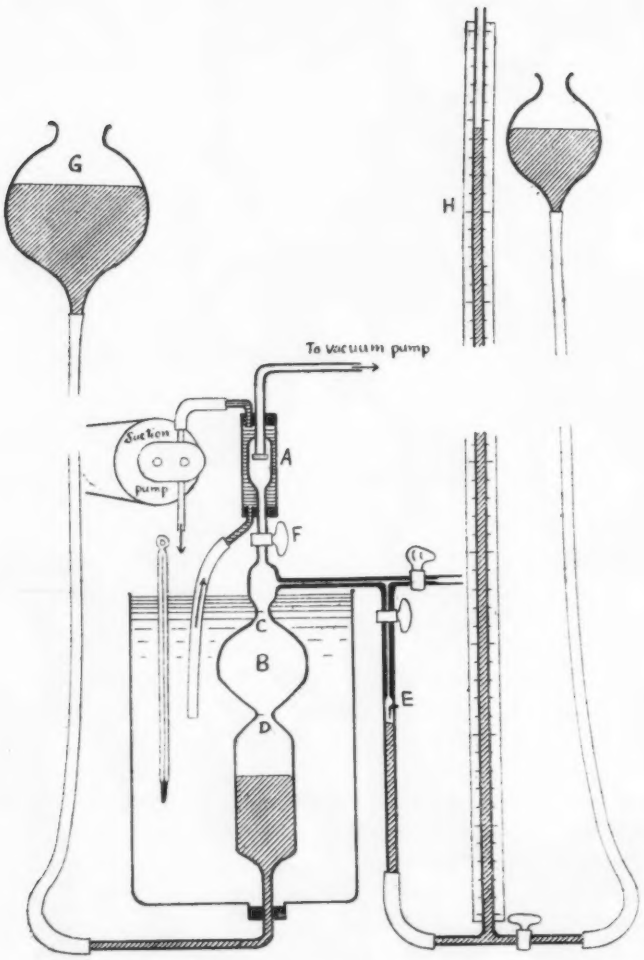


Fig. 1.

The gases examined were methane, ammonia, acetylene, ethylene, air, oxygen and carbon dioxide. All gases except air and oxygen were purified by washing with appropriate reagents and then fractionated by using the liquid air. Oxygen was made from potassium permanganate and passed through the tubes of calcium chloride, potassium hydroxide and phosphorus pentoxide. The results are shown in the following table. Moreover, the

time of flow through a perforated platinum plate under one atmospheric pressure has been measured, and the results are also shown in the same table.

Gas.	Time of effusion through an unglazed earthenware, in seconds.				Time of effusion through a perforated Pt. plate.	Mol. weight of gas.
	1.0 atm.	1.5 atm.	2.0 atm.	2.5 atm.		
Methane	962	785	664	573	176.2	16.037
Ammonia	944	762	637	548	178.4	17.032
Acetylene	1048	830	685	583	216.0	26.026
Ethylene	1080	849	700	599	225.7	28.042
Air	1414	1169	1003	878	230.9	28.96
Oxygen	1521	1268	1090	956	243.4	32.000
Carbon dioxide	1457	1162	968	829	279.4	44.005

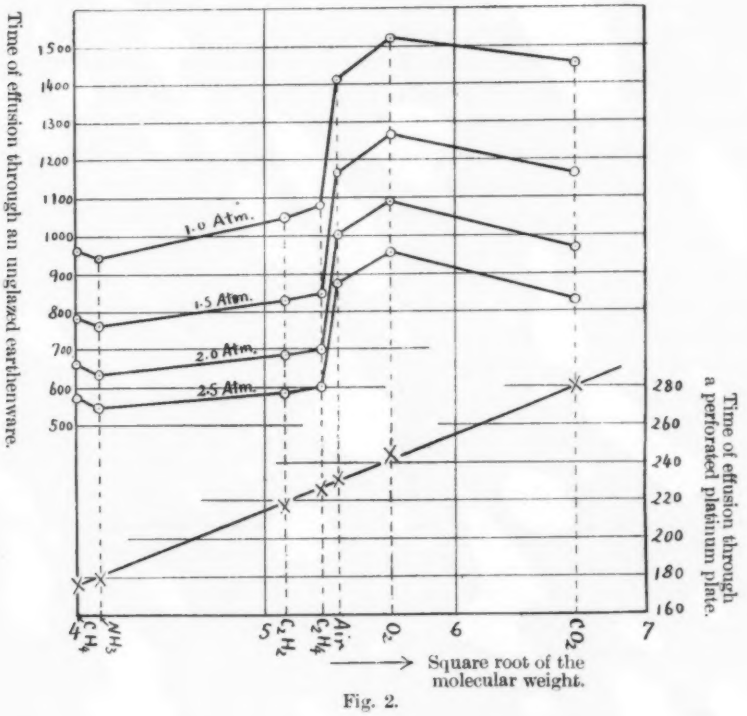


Fig. 2.

In Fig. 2 the square root of the molecular weight of gas is taken as abscissa and the time of effusion as ordinate. The circlets show the times of effusion through an earthenware under the pressures of 1.0, 1.5, 2.0 and 2.5

atmospheres, and the values corresponding to the same pressure are connected by straight lines. The results are far from expressed by the equation $t=k\sqrt{M}$. The crosses show the time of effusion through a perforated platinum plate. They lie nearly on a straight line, which means that they can be expressed by the above equation.

The time of effusion through an unglazed earthenware t will be expressed by the following equation,

$$t=k\eta^{n}M^{\frac{1-n}{2}}$$

where η is the viscosity coefficient of the gas, M is the molecular weight and k and n ($n<1$) are two constants independent of the kind of gas but depend on the nature of the porous wall and the pressure of gas. If the wall be very thin then n approaches to zero and the equation takes the usual form $t=k\sqrt{M}$, while if the wall be very thick (or a long capillary tube) then n tends to one and the equation becomes $t=k\eta$.

In the present experiment I have calculated the times of effusion from the above equation and the results are given in the following table. The values of the viscosity coefficients at 25° have been obtained by interpolations from the observed values of numerous authors at various temperatures.

Gas.	Viscosity coeff. at 25°.	Time of effusion calculated from the above equation.			
		1.0 atm. $k=24100$ $n=0.44$	1.5 atm. $k=50400$ $n=0.53$	2.0 atm. $k=79800$ $n=0.59$	2.5 atm. $k=104600$ $n=0.63$
Methane	1118×10^{-7}	957	779	657	566
Ammonia	1042 "	943	761	638	548
Acetylene	1030 "	1057	835	691	588
Ethylene	1015 "	1072	844	696	592
Air	1850 "	1409	1168	998	868
Oxygen	2080 "	1525	1273	1092	951
Carbon dioxide	1550 "	1465	1174	980	838

The differences between the observed (former table) and the calculated values (latter table) are within one percent excepting only a few cases.

Laboratory of Physical Chemistry,
Faculty of Science, Tokyo Imperial University.

ON THE ABSORPTION SPECTRA OF SALT SOLUTIONS OF SOME RARE EARTH ELEMENTS.[1]

By Toshi INOUE.

Received November 20, 1925. Published January 28, 1926.

It is the well known fact that some salts of rare earth elements yield highly characteristic absorption spectra, by means of which, therefore, they are very conveniently detected. Concering to this subject we have indeed plenty of literatures to be referred;[2] notwithstanding I repeated the study of the absorption spectra of some rare earth salts, in order to know whether their spectra are influenced from each other by mixing them and further to investigate the absorptions in the ultraviolet region, which are wanting in the preceding studies.

Experimental.

1) Absorption Spectra of Chlorides of Lanthanum, Cerium, Praseodymium, Neodymium, Samarium and Erbium in the Visible Region.

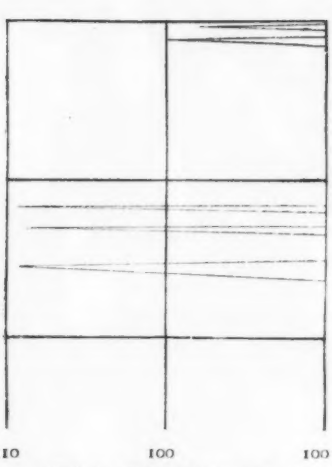
Lanthanum chloride, being colourless, shows no absorption band in the visible part. Cerous chloride also shows no bands, but its end absorptions are extended to the region of the spectrum of comparatively long wave lengths: namely 10 cm. layer of its 0.05 mol aqueous solution absorbs even to 4200 Å (violet), and 0.2 mol solution (the same thickness of layer) absorbs to 4600 Å (blue violet). The aqueous solutions of praseodymium chloride, neodymium chloride, samarium chloride and erbium chloride absorb remarkably in visible part and they show very characteristic bands, which accord very well with the results attained by the works already published.

Brauner and others[3] have studied the mutual influences of the absorption spectra of the solutions of rare earth salts, when they were mixed with each other. According to them, the spectra change distinctly their appearances by contamination of other salts. But in my present investigation, this was by no means the case; I studied, with the special care, the absorption bands 4441 Å of praseodymium, 5222, 5205, 5123 and 5091 Å of neodymium and 4071 and 4013 Å of samarium in mixing the salt solutions to each other or adding lanthanum chloride to each solution. These characteristic bands, however, remained always unchanged, and it was thus accertained that these elements may at least be detected by means of these absorption bands. (Fig. 1).

(1) Read before the Chemical Society of Japan, April 8, 1923.

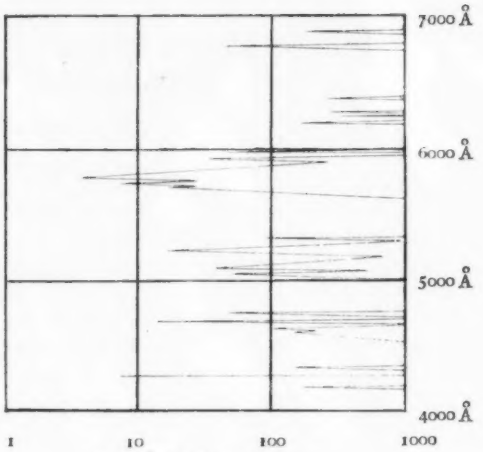
(2) Compare "A Text Book of Inorganic Chemistry" by N. Friends, Vol. IV, p. 283, (1917).
W. Prandtl, *Z. anorg. Chem.*, 116 (1921), 96.
Z. F. Yntema, *J. Am. Chem. Soc.*, 45 (1923), 907.

(3) B. Brauner, *J. Chem. Soc.*, 43 (1883), 278.
E. Demarçay, *Compt. rend.*, 126 (1898), 1039.



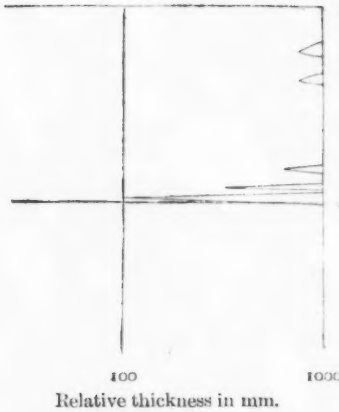
Relative thickness in mm. of 0.0256 mol solution

Praseodymium chloride.



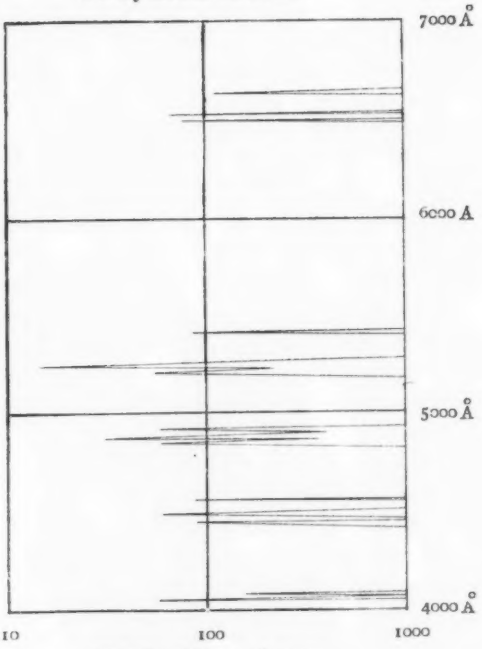
Relative thickness in mm. of 0.06 mol solution

Neodymium chloride.



Relative thickness in mm. of 0.011 mol solution

Samarium chloride.



Relative thickness in mm. of 0.02 mol solution

Erbium chloride.

Fig. 1.

2) Absorption Spectra in the Ultra-Violet Region.

Among chlorides of six rare earth elements above mentioned, only three, namely cerous chloride, samarium chloride and erbium chloride, show absorption bands in the ultra-violet region. As it will be seen in Fig. 2, cerous chloride possesses two bands, while both of samarium chloride and erbium chloride show only one in ultra-violet. The positions of their absorption maxima are given in the following table:

	Concentration in mol.	Thickness of liquid layer (cm.)	λ(Å)	ν
$CeCl_3$	0.01	2.8	3350	2985
	0.001	4.8	2469	4050
$SmCl_3$	0.11	1.4	2600	3850
$ErCl_3$	0.2	5.6	2470	4050

Chlorides of praseodymium, neodymium and lanthanum absorb only continuously in ultra-violet (compare Fig. 2.)

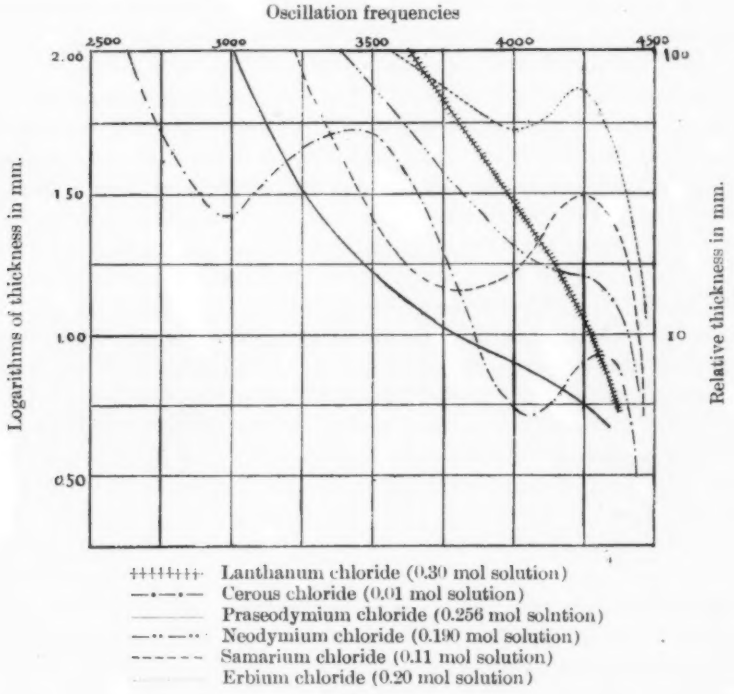


Fig. 2.

3) Application of Absorption Spectra for the Quantitative Determination of Some Rare Earth Elements.

The concentration of some rare earth salts in a solution may be determined by measuring the thickness of the liquid layer, at which a certain characteristic band of that element just disappears, provided that the limiting concentration (or the thickness of liquid layer) of disappearance of the same band at the certain thickness of liquid layer (or at the certain concentration) is previously known.

According to my present study, this method of analysis is especially suited for such the rare earths, that show absorption bands in the ultra-violet region, because the latters are, as a rule, far more wide and distinct than those of the visible part. For example, cerous chloride absorbs selectively very wide region of spectrum in ultra-violet; its analysis by using this method, therefore, will be scarcely hindered by the presence of other rare earth salts, which absorb likewise selectively in ultra-violet. In applying Beer's law, it was calculated from the experimental results that the quantity of cerous chloride in a given solution may be determined even when its fifty times so much praseodymium and samarium salts and its hundred times so much lanthanum and neodymium salts are simultaneously presented in that solution. In the actual case of mineral analysis, if the total quantity of the salts of lanthanum, praseodymium, neodymium and samarium do not exceed hundred times of that of cerous salt, the latter will be conveniently and rapidly determined by this spectroscopic method in performing as follows: the fraction of cerium group extracted from a given mineral will be changed into chlorides and the absorption spectra of that solution in various thicknesses of liquid layer are photographed on a same plate. The absorption curve will then be traced according to the Hartley-Baly's system and the thickness of liquid layer at the bottom of the absorption curve is measured. On the other hand, the absorption curve of cerous chloride of the known concentration will be prepared for the purpose of comparison, and on this curve, the thickness of liquid layer at bottom of the same absorption band is likewise determined. According to the Beer's law, the following simple relation will be given to denote the concentration of cerous chloride in the mineral extract:

$$c' = \frac{cl}{l'}$$

where c and c' mean respectively the concentrations of known and unknown solutions of cerous chloride, and l and l' are respectively the thicknesses of liquid layer of these solutions, at which the absorption bands just disappear.

For the purpose of the verification of this method, the following experi-

ment was carried out: a solution, containing 0.02 gr. CeO_2 and 1.1240 gr. R_2O_3 (R= metals of Ce-group, Ce itself excluded) in a litre as chlorides, was prepared, and the absorption spectrogram of this solution was made as usual. The absorption curve showed that the bottom of the band, the wave lengths of which is found 2469 Å, appears at the thickness of 4.0 cm. of liquid layer, while in the control solution, which contains 0.017 gr. of CeO_2 as chloride in a litre, the bottom of the same absorption band was found at the thickness of 4.8 cm. of liquid layer. The quantity of CeO_2 in the first solution will, therefore, be calculated from the following formula.

$$\frac{4.8 \times 0.0170}{4.0} = 0.0204.$$

As for the ultra-violet absorption of samarium chloride, it is not interfered by that of lanthanum chloride, but when the quantities of the coexisting neodymium and praseodymium chlorides exceed respectively 3 and 1 times of that of samarium chloride, the characteristic absorption band at 2600 Å of the latter salt is no more of without influence. In the practice, therefore, the spectrogram of the solution of rare earths fraction extracted from a certain mineral will be carefully examined, and if the band of samarium 2600 Å be found therein, so we can at least conclude that the extract contains neodymium in the less quantity than 3 times that of samarium and praseodymium less than the equal quantity of samarium. In this case, therefore, the above mentioned method may be applied for the quantitative analysis of the latter element utilising its characteristic band.

Summary

1) The absorption spectra of chlorides of lanthanum, cerium (trivalent), praseodymium, neodymium, Samarium and erbium were studied and compared with the works published up to the present time.

2) In studying the ultra-violet absorptions of these salts, the existence of the following bands was confirmed:

3350 and 2469 Å in cerous chloride; 2600 Å in samarium chloride; 2470 Å in erbium chloride.

3) A method for the quantitative analysis for cerium and samarium by measuring their characteristic ultra-violet absorptions was described.

I express my hearty thanks to Prof. Yuji Shibata for his kind advices.

The cost of the investigation was defrayed from the grant of the Department of Education.

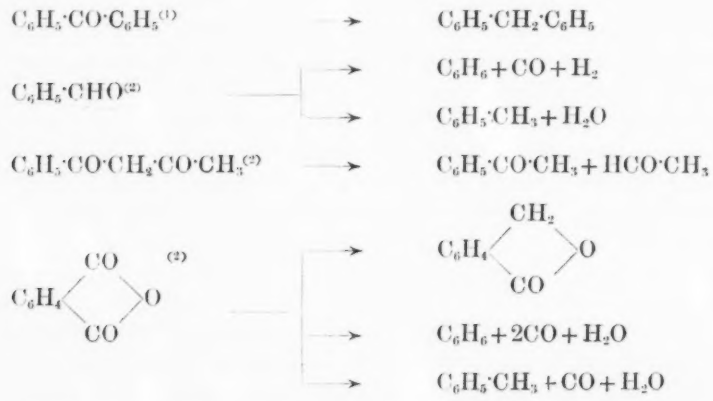
Laboratory of Inorganic Chemistry,
Faculty of Science, Tokyo Imperial University.

ON THE CATALYTIC HYDROGENATION OF THE CARBONYL GROUP IN AROMATIC COMPOUNDS UNDER PRESSURE IN THE PRESENCE OF COPPER. PART I.

By **Bennosuke KUBOTA** and **Taro HAYASHI.**

Received December 4, 1925. Published January 28, 1926.

It has been shown by P. Sabatier and his collaborators that the carbonyl group in aromatic compounds undergoes a violent hydrogenation in gaseous system in the presence of copper, giving rise to the formation of hydrocarbons or even to the scission of the molecule, and that it is impossible in general to get any alcohol from aldehyde or ketone by this process of hydrogenation.

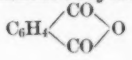
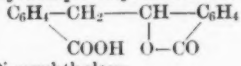
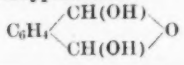


On the other hand, Aloy and Brustier[3] have shown that borneol changes into camphor almost perfectly at 300° in the presence of this catalyst. These facts naturally lead one to suppose that, as copper is, under ordinary pressure, evidently a suitable catalyst for dehydrogenation of the carbinol group rather than for hydrogenation of the carbonyl group, the reverse reaction would take place under high pressure;

$$-CH(OH)- \rightleftarrows -CO- + H_2.$$

(1) P. Sabatier et Murat, *Compt. rend.*, 158 (1914), 761.
(2) P. Sabatier et B. Kubota, *Compt. rend.*, 172 (1921), 733.
(3) Aloy et Brustier, *Bull. Soc. Chem.*, 9 (1911), 733.

This view has been found to be correct from the following experiments. Diketones (benzil, benzoyl acetone, and phthalic anhydride) and monoketones (acetophenone, benzophenone and camphor) were hydrogenated in an autoclave by means of hydrogen under high pressure in the presence of this catalyst, all producing expected products. It was found, moreover, that two new compounds, methyl-(β-phenyl-β-oxy-ethyl)-ketone $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$ and dioxyphthalane $C_6H_4[CH(OH)]_2O$, were obtained from benzoyl acetone and phthalic anhydride. The results may be summarized as follows:

	Substance	Temperature of the oil bath	Pressure (atm.) initial	max.	Product
Diketone	Benzil $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$	100°	76	92	Benzoin $C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_5$ Hydrobenzoin and Isohydrobenzoin $C_6H_5{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_6H_5$
		130	64	80	Hydrobenzoin and Isohydrobenzoin
	Benzoyl acetone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COCH_3$	83	68	79	Phenyl-(β-oxy-n-propyl)-ketone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$ Methyl-(β-oxy-β-phenyl)-ketone $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$
		105°	57	69	α-Methyl-γ-phenyl-trimethylene glycol $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$
	Phthalic anhydride 	120	67	82	Hydrodiphthalyl lactonic acid  Dioxyphthalane 
Monoketone	Acetophenone $C_6H_5{\cdot}CO{\cdot}CH_3$	140	66	86	Phenyl-methyl carbinol $C_6H_5{\cdot}CH(OH){\cdot}CH_3$
		160	66	96	Phenyl-methyl-methane $C_6H_5{\cdot}CH_2{\cdot}CH_3$
	Benzophenone $C_6H_5{\cdot}CO{\cdot}C_6H_5$	120	50	61	Diphenyl carbinol $C_6H_5{\cdot}CH(OH){\cdot}C_6H_5$ Diphenyl methane $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$
		190	52	67	Diphenyl methane $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$ Tetraphenyl ethane $(C_6H_5)_2{:}CH{\cdot}CH{:}(C_6H_5)_2$
	Camphor $C_{10}H_{16}O$	120–150	10–90	19–101	Borneol and Isoborneol $C_{10}H_{18}O$

Experiments with diketones are described in this paper, and those with monoketones will be published in the next communication.

Experimental.

The substance to be hydrogenated was mixed intimately in a pyrex glass tube with about half its weight of fine copper of purple colour, which had been prepared from precipitated cupric hydroxide by the reduction with a very slow current of hydrogen at about 180°. It was placed in the autoclave, to which hydrogen under 60–76 atmospheres was introduced and was heated in an oil bath about 18–30 hours. When the reaction was completed, the whole mass in the pyrex glass tube was shaken up with either, and the ethereal solution was filtered from the catalyst. The solution, after being dehydrated over anhydrous sodium sulphate, was distilled to expel ether, and the product remaining in the flask was examined.

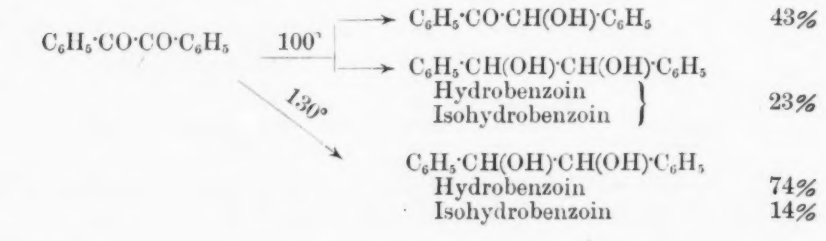
1. Benzil $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$.

Being treated at 100° (the temperature of the oil bath) under 60 atmospheric pressure (initial) as above mentioned, the mixed product was treated with hot dilute alcohol and was filtered while still hot. Faintly yellow crystals were obtained, which melted at 132° and was identified as benzoin.

To this hot filtrate some hot water was added gradually so long as yellowish oil, which was proved to be unchanged benzil, separated out, and the hot solution was filtered off. When the filtrate was cooled, large crystals separated out. This was found to melt at 134–135° and to possess the characteristic properties of hydrobenzoin, its diacetate being formed by the action of glacial acetic acid on it at 170–180° and so forth.

After filtering the hydrobenzoin, the volume of the filtrate was diminished by evaporation on a water bath, when some crystals of hydrobenzoin again separated out. This was filtered off while still hot and the filtrate was allowed to stand over night. Then some crystals separated out in needles. This substance melted at 94–95° and proved to be isohydrobenzoin.

Similar experiments with benzil was undertaken at about 130° under 64 atmospheric pressure, the products were found to be hydrobenzoin and isohydrobenzoin. Thus the results obtained with benzil may be represented in the following scheme:



2. Benzoyl acetone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

This was treated at 83–87° (the temperature of the oil bath) under 68 atmospheric pressure (initial) as above mentioned. A large quantity of crystalline substance, which proved to be nothing but unchanged benzoyl acetone, and a colourless viscous liquid with a good smell were obtained. The liquid was filtered, fractionated under 12 mm. pressure, and the following fractions were collected: 125–135° (3%), 135–136° (30%), 150–153° (4%).

The first fraction was found to be nearly pure unchanged benzoyl acetone (melting point, 48°) dissolved in the liquid. The second fraction was shaken up with a dilute caustic soda solution so long as it showed any marked ferric chloride reaction, in order to elliminate a trace of benzoyl acetone. Then the liquid was extracted by means of ether. The ethereal solution, on being dehydrated over anhydrous sodium sulphate and evaporated, gave a liquid boiling at 134–136° under 10 mm. pressure, which on analysis proved to be a new oxyketone. (Found: C=73.23; H=7.99. $C_{10}H_{12}O_2$ requires C=73.15; H=7.32 per cent).

The liquid produced an yellow turbidity on the addition of a solution of phenylhydrazine in acetic acid, which precipitated together after a few hours. This was filtered and recrystallised from alcohol. It formed orange crystals melting with partial decomposition at 120–122°. (Found: C=74.80; H=7.01; N=11.35. $C_{16}H_{18}N_2O$ requires C=75.59; H=7.14; N=11.01 per cent).

When it was warmed for some time with acetyl chloride on a water bath, it turned into a colourless viscous liquid with a very good smell.

These facts show that the product is evidently an oxyketone, suggesting as its constitution either of the two following formulae:

$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$ (1), $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (2).

By the condensation of acetophenone with acetaldehyde, Staudinger and Kon[1] obtained a viscous liquid boiling at 150–153° under 12 mm. pressure, which proved to be phenyl-(β-oxy-n-propyl)-ketone (1). The properties of the third fraction were found to be in good agreement with those of the oxyketone of Staudinger and Kon.

It is now clear that the second fraction is a new oxyketone represented by the formura (2): $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

In the course of their investigation on catalytic hydrogenation of several aliphatic-aromatic carbonyl compounds in presence of palladium, Straus and Grindel[2] have shown that the hydrogenation of those compounds in which the carbonyl group is in the α-position to the benzene ring is carried out more quickly than the other carbonyl compounds. Our result with benzoyl

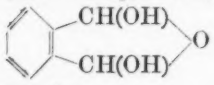
(1) Staudinger and Kon, *Ann.*, 384 (1911), 124.
(2) Straus and Grindel, *Ann.*, 439 (1924), 276.

acetone is obviously in complete agreement with that of Straus and Grindel, being represented by the following scheme:

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COCH_3 \longrightarrow \begin{cases} C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO.CH_3 & 30\% \\ C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3 & 4\% \end{cases}$$

Benzoyl acetone was next treated at 105° under 57 atmospheric pressure. The product was a liquid which was fractionated under 12 mm. pressure and the following fractions were collected: 135–160° (very little), 162–166° (70%), 167–172° (25%). The properties of the second fraction were found to be in good agreement with those of α-methyl-γ-phenyl trimethylene glycol. $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$, of E. Bauer.[1]

3. Phthalic anhydride $C_6H_4\begin{<}\begin{matrix}CO\\O\\CO\end{matrix}\!\!>$.

This was treated at 120° under 67 atmospheric pressure (initial) and the result was, that a large quantity of white crystals and some green viscous liquid were obtained. This was drained on a funnel with a perforated plate and the filtrate was shaken up with dilute hydrochloric acid when the green colour of the liquid disappeared. This was washed several times with a dilute sodium carbonate solution, then with water, and extracted with ether. The ethereal solution was dehydrated over anhydrous sodium sulphate and the ether was distilled off, when a colourless liquid was obtained. (Found: C=63.95; H=5.32. $C_8H_8O_3$ requires C=63.15; H=5.31 per cent). Thus it seems to us that this is a dioxyphthalane, 
which has not yet been obtained by any other reaction.

On being treated with benzoyl chloride and sodium hydroxide solution, it gave a viscous liquid which smelled fragrant and was ascertained by analysis to be dibenzoyl ester of dioxyphthalane. (Found: C=73.31; H=4.26. $C_{22}H_{16}O_5$ requires C=73.30; H=4.44 per cent).

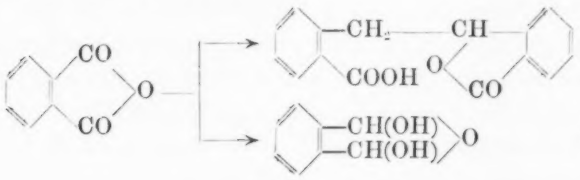
The crystalline substance above described, on being recrystallised from alcohol, separated out in colourless plates melting at 197–198°. Its properties were found to be in good agreement with those of hydrophthalyl lactonic acid of Wislicenus.[2]

As it is known that the phthalic acid and its derivatives are apt to change into phthalic anhydride on being oxidised by air when heated, the

(1) E. Bauer, *Compt. rend.*, 154 (1912), 1093.
(2) Wislicenus, *Ber.*, 17 (1884), 2178.

dioxyphthalane and its benzoyl ester have not been distilled, because they will be decomposed into phthalic anhydride even under 5 mm. pressure.

Now the hydrogenation of phthalic anhydride by this process may be represented by the following scheme:



70% Hydrodiphthalyl lactonic acid of Wislicenus

12% Dioxyphthalane, a new compound.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.

ÜBER DIE ANHYDRISIERUNG VON AMINOSÄUREN UND PEPTIDEN. (EINE ANTWORT AN HERRN ABDERHALDEN.)

Von **Keita SHIBATA.**

Eingegangen am 14. Dezember 1925. Ausgegeben am 28. Januar 1926.

In einem kürzlich erschienenen Aufsatz[1] hat Herr Abderhalden unter Bezugnahme auf meine Veröffentlichung[2] über den Glycerin-Abbau der Eiweisskörper folgendes geschrieben: „Shibata glaubt, dass die Anwendung von Glycerin jede sekundäre Umlagerung ausschliesse.....," und knüpfte daran die Beschreibung seiner Versuche über die Anhydridbildung aus einigen Di- und Tripeptiden durch Erhitzen mit Glycerin an. Es lag mir ganz fern eine ebensolche Behauptung aufzustellen, sodass ich genötigt bin, im folgenden einige Zeilen der Klarlegung der Sache zu widmen.

Was Herrn Abderhalden zur obigen unzutreffenden Bemerkung veranlasste ist wahrscheinlich folgender Satz[3] in meiner Mitteilung: „Da die oben beschriebene Methode[4] jede Möglichkeit der Hydrolyse ausschliesst, so ist es gar nicht an *sekundäre Entstehung* der Anhydride aus Aminosäuren

(1) Emil Abderhalden u. Ernst Schwab: Z. physiol. Chem., 148, 254. (Oktober 1925.)

(2) Keita Shibata: Acta Phytochimica, 2, 39. (April 1925.)

(3) Daselbst, 43.

(4) d.h., Depolymerisierung der Proteine durch Erhitzen mit wasserfreiem Glycerin.

und Peptiden zu denken." Wie leicht ersichtlich, wollte ich damit meinen, dass die Anhydride nicht erst aus hydrolytisch abgespaltenen Aminosäuren und Peptiden hervorgegangen sind, sondern vorgebildet in Proteinkörper existieren müssen. Derselbe Gedankengang liegt bekanntlich auch der Isolierung der Polysaccharidgrundkörper durch Glycerinabbau zu Grunde.

Die interessante Beobachtung Maillards über die Anhydridbildung aus Aminosäuren durch Erhitzen im Glycerin wurde bereits von mir bei der Darstellung von eiweissähnlichen kolloiden Polymeren benützt, wie in meiner oben zitierten Mitteilung angegeben.(1) Weiterhin sind die Versuche zur Herstellung verschiedener Diketopiperazinderivate nach der Maillardschen Methode schon lange von Dr. Teiichi Asahina in Angriff genommen, mit dem Zweck, die Identifizierung und Kennzeichnung der Proteingrundkörper zu erleichtern.

Selbstredend führen ich und meine Mitarbeiter weitere Untersuchungen in der schon angekündigten Arbeitsrichtung ungestört aus.

Bei dieser Gelegenheit möchte ich nochmals kurz auf die oben erwähnten eiweissähnlichen Substanzen hinweisen, die beim Erhitzen des Aminosäurengemisches mit wenig Glycerin entstehen.(2) Die betreffende Substanz wird, wie schon angegeben,(3) aus der alkoholischen Glycerinlösung beim Zusatz von kleinen Mengen von Oxyden, Neutralsalzen (Chloriden, Nitraten, Acetaten) sowie gewissen Komplexsalzen der Erdalkalimetalle(4) in voluminösen Flöckchen niedergeschlagen, und durch Waschen mit abs. Alkohol und Trocknen im Vakuum in der Form eines hellgelben amorphen Pulvers gewonnen. Die Substanz ist im Wasser spielend leicht löslich, enthält keine freie Aminosäuren, gibt nicht nur verschiedene Farben-,

(1) Dort (S. 45) schrieb ich: „Die oben dargestellten Versuche kann man auch mit freien Aminosäuren anstellen, da die letzteren, wie Maillard nachwies, beim Erhitzen im Glycerin in Anhydride übergeführt werden und dabei aus dem Gemisch zweier Aminosäuren auch ein ‚gemischtes' Anhydrid entsteht." Dass die Peptide dabei wie Aminosäuren verhalten, ist ja von vornherein zu erwarten.

(2) Die Association (Polymerisation) und Deassociation der Anhydriden im Glycerin stellen gewissermassen einen reversiblen Vorgang dar, der sich nach Konzentration, Temperatur und anderen Faktoren richten.

(3) K. Shibata: loc. cit., 45.

(4) Die Salze von Schwermetallen (Mn, Fe, Ni, Co, Zn, Cd, Cu, Ag, Hg) und Lanthan lassen sich ebensogut wie die von Erdalkalien dazu verwenden, aber die entstehenden Produkte sind oft im Wasser schwer oder kaum löslich. Die Verbindungen von Alkalimetallen sowie Mg, Be, Al u.a. sind nicht zum Versuch brauchbar.

sondern auch Fällungsreaktionen der Proteinkörper. Die prozentische Zusammensetzung variiert freilich nach dem Mengenverhältnisse der angewandten Aminosäuren. Der Aschengehalt der Präparate lässt sich auf Anlagerungsverbindungen der Metallsalze mit den polymeren oder assoziierten Anhydriden[1] schliessen. Aber die Substanzen können von Metallen weitgehend befreit werden, indem man, z. B., die letzteren in ammoniakalischer Lösung als Karbonate ausfällt, und aus dem Filtrat gewinnt man durch Alkoholfällung eine beinah aschefreie Substanz zurück. Die Entstehungsbedingungen und Eigenschaften dieser künstlichen pepton- oder albumoseartigen Substanzen werden a.a.O. näher beschrieben.

Botanisches Institut,
Kaiserliche Universität, Tokyo.

(1) Oder deren tautomeren Formen.